Crossed Molecular Beams Investigations on the Dynamics and Energetics of Elementary Boron Reactions with Unsaturated Hydrocarbons

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14. ABSTRACT
We have demonstrated the capability to carry out crossed molecular beams reactions of boron atoms with unsaturated hydrocarbons (here allene). It should be recalled that the AFOSR Grant FA9550-05-1-0124 under which the experiments have been conducted was intended as a starter grant to getthe eexperimental setup complete, the boron source optimized, and first data on boron atom reactions. Effective 8/1/2005, the crossed beams experiments as outlined under 'Objective' are continued under AFOSR graant W911NF-05-1-0448. In addition, we have finalized the design and construction of a new electron impact ionizer incorporating soft electron impact ionization utilizing tunable electron energies as low as 7 eV. This will enable us to detect potential small hydrocarbon radical fragments such as methyl, ethyl, vinyl, and ethynyl and also allows us to discriminate between isomers of the heavy reaction products formed via dicarbon versus atomic/molecular hydrogen exchange pathways if their ionization potentials are separated by about 0.5-0.75 eV. Currently, the operation conditions of this unit are tested in a separate UHV chamber.

15. SUBJECT TERMS

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1. Objectives

The objectives of this research program are to unravel experimentally the energetics and the collision energy dependent dynamics of the reactions of ground state boron atoms, $B(^2P_j)$, with acetylene ($C_2H_2(X^1\Sigma_g^+)$), ethylene ($C_2H_4(X^1A_g)$), methylacetylene ($CH_3CCH(X^1A_1)$), allene ($H_2CCCH_2(X^1A_1)$), and benzene (C_6H_6 (X^1A_{1g})) under single collision conditions employing a crossed molecular beams machine at the Department of Chemistry of *The University of Hawai'i*. The closed shell hydrocarbon molecules serve as prototype reactants with triple (acetylene), double (ethylene), and *aromatic* (benzene) carbon-carbon bonds; methylacetylene and allene are chosen as the simplest representatives of closed shell hydrocarbon species to investigate how the dynamics change from one structural isomer to the other. Within this program, the following objectives (O1-O3) will be pursued:

O1: To build a crossed molecular beams machine which incorporates a high intensity, supersonic boron atom source and a truly universal detection system utilizing angular resolved *tunable, soft electron impact ionization* of the reaction products.

O2: To carry out the proposed boron atom reactions and to collect data on the reaction products, their isomers, intermediates involved, and the collision energy dependent reaction dynamics.

O3: To incorporate these data into novel, boron-based combustion network investigating boron combustion processes and boron-based rocket propellants thus predicting the performance of combustion and propellant systems, and minimizing the emission of unwanted by-products, and ultimately optimizing the propulsion efficiency.

2. Relevance to AFOSR Sponsored Research

One of the prime interests of the AFOSR program is to sponsor combustion related research which provides data and procedures to enable the development of reliable chemical propulsion systems. The latter should be able to quantitatively predict the performance of combustion and propellant systems to minimize the emission of unwanted by-products and to maximize the propulsion efficiency. However, all combustion models require crucial input parameters such as the knowledge of rate constants of the chemical reactions over a wide temperature and pressure range, the identification of reaction intermediates, which either form products, are stabilized via three body reactions, react with other molecules, or decay back to the reactants, and the assignment of the primary reaction products together with branching ratios. At present this includes AFOSR sponsored research to understand, predict, and to control rocket propulsion systems and the reactivity and energy flow in molecular systems. Our research initiative connects to the *Combustion and Diagnostics* and *Space Power and Propulsion* programs aimed to untangle the chemistry of reacting flows of chemical propulsion systems in, for example, chemical rockets and ramjet engines. Based on these data, the ultimate goal is to predict and to eliminate combustion instabilities and to optimize the efficiency of chemically-based propulsion systems.

3. Accomplishments

3.1. Crossed Beams Machine, Supersonic Boron Source, & Ionizer

The main chamber of the crossed beams machine consists of a 304 stainless steel box (180 cm × 160 cm × 80 cm; 2300 l; machining accuracy: ± 0.03 mm) and is evacuated by three 2000 ls^{-1} magnetically suspended turbo molecular pumps (Osaka Vacuum; TG 2003) backed by a single scroll pump (Edwards XD35; 10 ls^{-1}) to the low 10^{-8} torr region (Figures 1 and 2). To reduce the background from straight-through molecules into the detector, the machine is also equipped with a cold shield located between the interaction region and the chopper wheel (primary source) and downstream the skimmer (secondary source). This oxygen free high conductivity (OFHC) copper shield (10 K) is interfaced to a CTI CP-1020 cold head and improves the vacuum in the main chamber to 4×10^{-9} torr. Two source chambers are located inside the main chamber; in its current geometry, both beams cross perpendicularly. Each source chamber is pumped by a 2000 ls^{-1} and a 430 ls^{-1} maglev pump (Osaka Vacuum; TG2003 and TG430) to the low 10^{-8} torr region; the operation of pulsed and continuous sources increases the pressure to about 10^{-5} torr and 10^{-4} torr, respectively. All maglev pumps require no maintenance and are hydrocarbon free. A dry roots pump (Leybold WS505; 140 ls^{-1}) roughed by two oil-free EcoDry M30 pumps (Leybold; 16 ls^{-1}) backs the turbo pumps of each source chamber. To minimize the outgasing of the sealing material, copper gaskets are used preferentially. Whenever O rings are used (detector entrance port, laser entrance window, main door), these are teflon-coated and differentially pumped by an oil-free pumping station at 10^{-7} torr to ensure the 4×10^{-9} torr in the main chamber.

Pulsed boron atom beams were produced in the primary source by laser ablation of boron at 266 nm (10 mJ per pulse at 30 Hz). The ablated species were seeded in neat carrier gas (helium, neon, or argon, 99.9999 %, 3040 torr) released by a Proch-Trickl pulsed valve. After passing a skimmer, a four-slot chopper wheel mounted after the ablation zone selected a part out of the seeded boron beam which crossed then a pulsed hydrocarbon beam under a well-defined collision energy in the interaction region.

The reactively scattered species are monitored using a quadrupole mass spectrometer. The detector is located in a separate, triply differentially pumped ultra high vacuum chamber and is rotatable within the plane defined by both beams. Since every rotation in a vacuum system will increase the pressure, the rotating detector ring is separated by three teflon loaded seals from the atmosphere. The spaces between these seals are doubly differentially pumped to reduce the pressure from atmosphere (760 torr) via 10^{-2} torr and 4×10^{-8} torr (teflon sealed regions) to 4×10^{-9} torr in the main chamber. This arrangement ensures no pressure increase in the main chamber even when the detector is being rotated. Differentially pumped detector regions I/II reduce the gas load from the main chamber, whereas region III contains the Brink-type electron impact ionizer surrounded by a liquid nitrogen cold shield. The quadrupole mass filter and the Daly-type scintillation particle detector are connected to region II. Each region is pumped by a magnetically levitated turbo molecular pump (region I/II: TD411, 430 ls^{-1}; region III: TD 400: 300 ls^{-1}); all three pumps are backed by a 430 ls^{-1} turbo molecular pump whose exhaust is connected to an oil free scroll pump (Edwards XD35; 10 ls^{-1}). This pumping scheme reaches down to the low 10^{-11} torr in region III; lower pressures can be achieved by operating a cold head inside region

III (Sumitomo; RDK-415 E; 4 K; 1.5 W). A slide valve with a teflon coated O-ring (Kalrez 117) is used to separate the main chamber from the first differentially pumped detector region. The regions are separated by rectangular apertures. During on-axis operation (beam characteristics) a small detector aperture of 0.25 mm is used, whereas off-beam-axis scattering experiments require a larger, 3.81 mm × 3.81 mm rectangular aperture. Here, the 5.8 mm × 5.8 mm rectangular aperture of region III constrain the viewing angle of the ionizer to 0.74° in each direction defining the detector acceptance angle to 6.7 ± 0.2 × 10^{-4} sr. Recall that despite the detector's differential pumping setup, molecules desorbing from wall surfaces lying on a straight line to the electron impact ionizer (straight-through-molecules) cannot be avoided since the mean free path of these species is in the order of 10^3 m compared to maximum detector dimensions of about 1 m. To reduce this background contribution, a copper plate attached to a two stage closed cycle helium refrigerator is placed right before the collision center; this unit is cooled down to 10 K; two holes of diameters of 2.5 mm allow the molecules to pass from the source chambers through the skimmer and the cold shield aperture to cross in the interaction region. Since the copper shield is located between the two skimmers and the scattering region, the ionizer 'views' a cooled surface which traps all the species with the exception of H_2 and He.

The home made Brink-type ionizer consists of a thoriated iridium filament - spot welded to a gold plated stainless steel electron repeller cup and a gold plated stainless steel plate - a meshed wire grid (0.25 mm diameter gold wire), as well as extractor and focus lenses. Extracted ions are focused by an electric lens located after the extractor plate enter the ionizer exit aperture, pass the quadrupole mass filter, and are accelerated towards a stainless steel target coated with a 200 nm aluminum layer maintained at -25 kV. The ion hits the surface and initiates an electron cascade which is accelerated by the same potential until they reach an aluminum coated (200 nm) organic scintillator whose photon cascade is detected by a photomultiplier (PMT) mounted outside the UHV detector. The PMT tube is operated at negative voltages between - 1100 V and 1350 V. Each PMT-pulse passes a discriminator set between 2.0 and 2.5 mV to eliminate low-level noise and is amplified. Here, an amplification by the PMT dynode chain of about 3 × 10^7 combined with a pulse width of about 10^{-8} s produces a current of about 0.5 mA. A 50 Ω termination gives rise to pulse amplitudes of 20 mV. This calculation suggest that our experimentally determined discriminator setting is a reasonable value. - The TTL pulse is fed into the multi channel scaler (time-of-flight spectra (TOF); dwell time between 0.64 μs and 10.24 μs) or the MERLIN module (Extrel) (residual gas analyzer mode). The operation potentials of the ionizer have been optimized as follows: extractor: -55 V; focus lens: 0V; electron energy (the potential difference between the electron repeller cup and the grid): 200 eV; ion energy (potential difference between the grid and the quadrupole rods): 36 eV. We also added the following components to the ¾'' quadrupole rod system: i) a grounded quadrupole housing, ii) quad pre- and post filters (0 – -2 V), and iii) entrance and exit lens (- 40 V). These settings improved the sensitivity of our system by a factor of about 20-30. In addition, we incorporated a four lead circuit, i.e. feeding two instead of one wire to the anode and cathode of the thoriated iridium filament. This circuit eliminates the resistance of the leads to the filament and hence minimizes voltage drops. The reduced voltage drop in turn minimized the heat released from the filament to typically 6.3 VA (1.8 V and 3.5 A for 1 mA emission current).

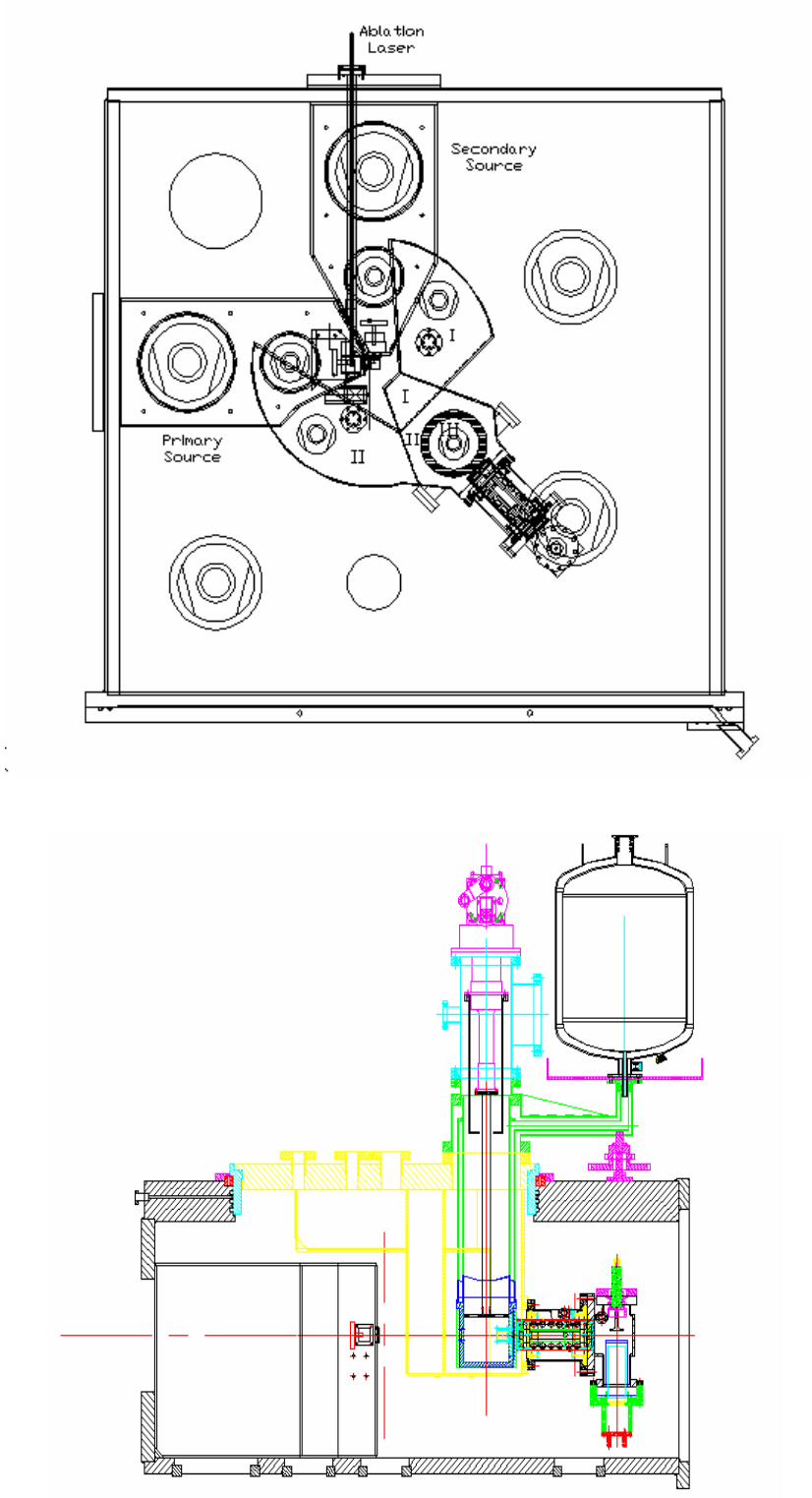

Figure 1: (Top) Top view of the experimental setup with differentially pumped regions I – III, source chambers, chopper wheel, ablation source, and laser channel. (Bottom) Side view of the main chamber and of the rotatable detection system of the crossed beams setup with differentially pumped regions I – III, the ionizer (region III), quadrupole rod system (region II), Daly detector (region II), photomultiplier tube (PMT), liquid nitrogen jacket (region III), and cold head (region III).

3.2. Crossed Beams Experiments

We were able to conduct successfully the crossed beams reaction of boron atoms with allene at a collision energy of 15 kJmol^{-1}. A conversion of the data from the laboratory to the center-of-mass frame lead to the discovery of the born atom versus atomic hydrogen exchange pathway to form two distinct isomers of the molecular formula C_3H_3B via indirect scattering dynamics (Figures 2-4). Note that neither molecular hydrogen elimination, nor hydrogen abstraction, nor boron-carbon skeleton fragmentation pathways were observed in this system. As this final report is written up, electronic structure calculations on the energetics of distinct C_3H_3B are carried out so that we can assign the nature of two reaction products and elucidate their formation pathways and hence the underlying reaction dynamics.

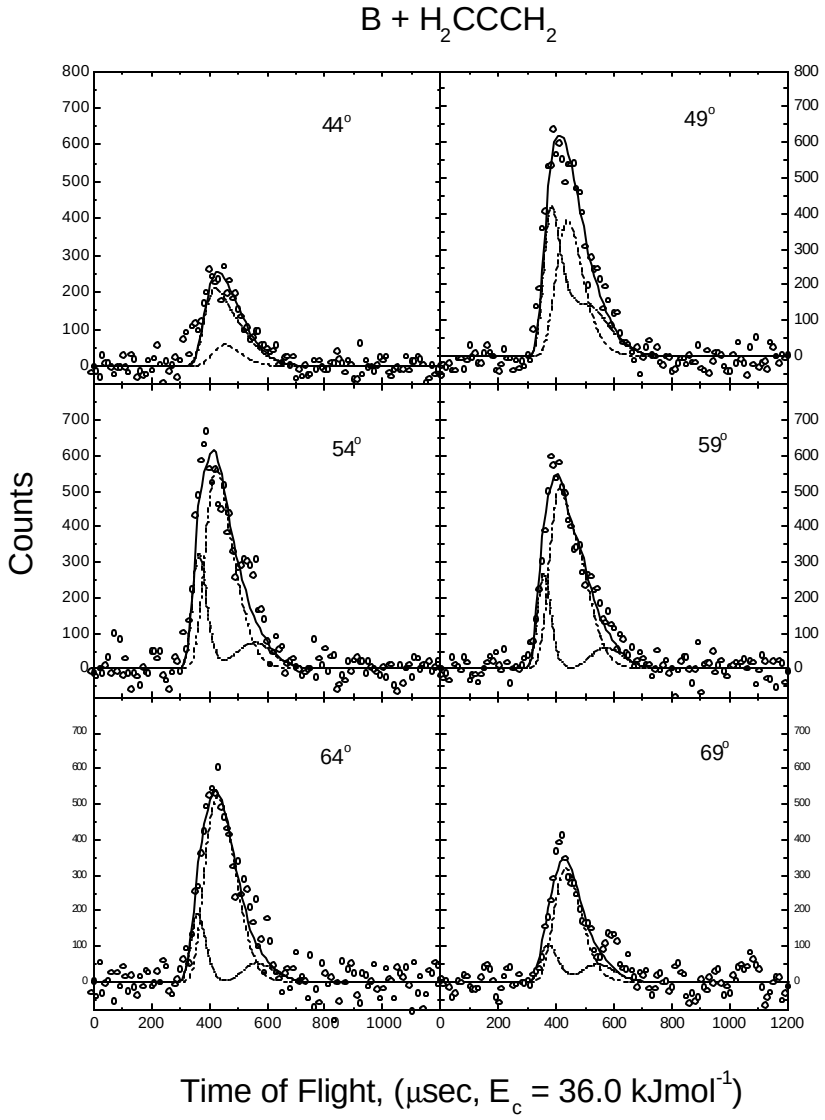

Figure 2: Selected time-of-flight spectra (TOF) of the C_3H_3B product recorded at a mass-to-charge ratios (m/z) of m/z = 50 (C_3H_3B).

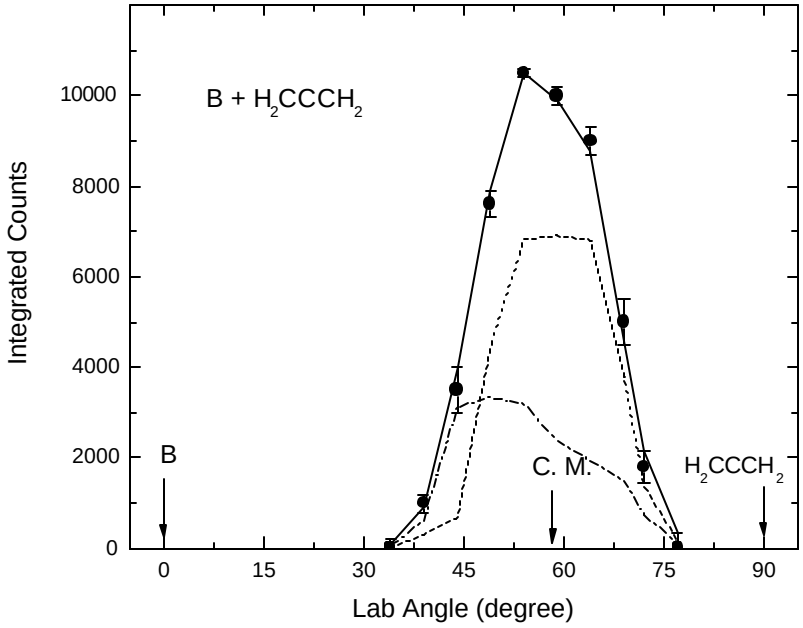

Figure 3: Laboratory angular distribution for the reaction of boron atoms with allene. The corresponding center-of-mass functions contributing to both product isomers are shown in Figure 4.

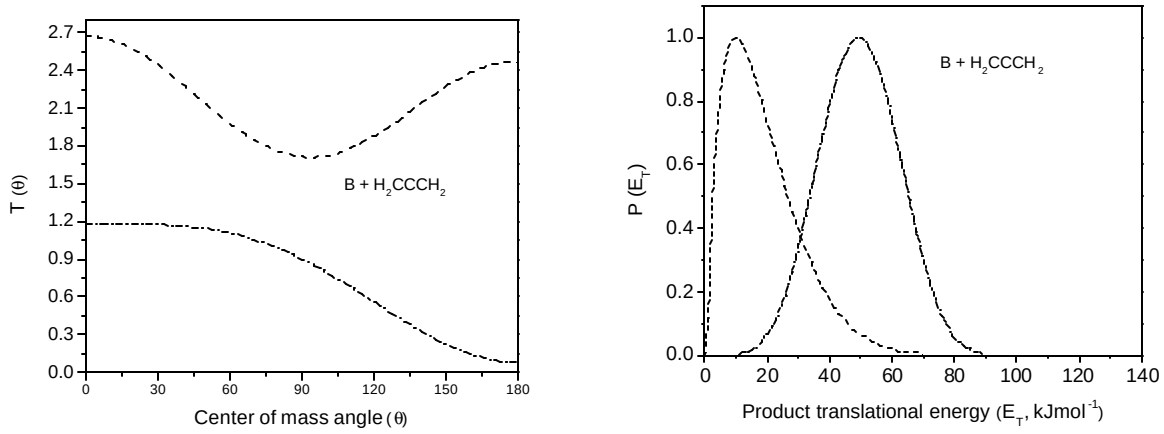

Figure 4: Center-of-mass angular (left) and translational energy (right) distributions of two micro channels leading to the formation of C_3H_3B isomers plus atomic hydrogen

3.3. Outlook

We have demonstrated the capability to carry out crossed molecular beams reactions of boron atoms with unsaturated hydrocarbons (here: allene). It should be recalled that the AFOSR Grant FA9550-05-1-0124 under which the experiments have been conducted was intended as a starter grant to get the experimental setup complete, the boron source optimized, and first data on boron atom reactions. Effective 8/1/2005, the crossed beams experiments as outlined under '*Objectives*' are continued under AFOSR grant W911NF-05-1-0448. In addition, we have finalized the design and construction of a new electron impact ionizer incorporating soft electron impact ionization utilizing tunable electron energies as low as 7 eV. This will enable us to detect potential small hydrocarbon radical fragments such as methyl, ethyl, vinyl, and ethynyl and also allows us to discriminate between isomers of the heavy reaction products formed via dicarbon versus atomic/molecular hydrogen exchange pathways if their ionization potentials are separated by about 0.5-0.75 eV. Currently, the operation conditions of this unit are tested in a separate UHV chamber (Figure 5).

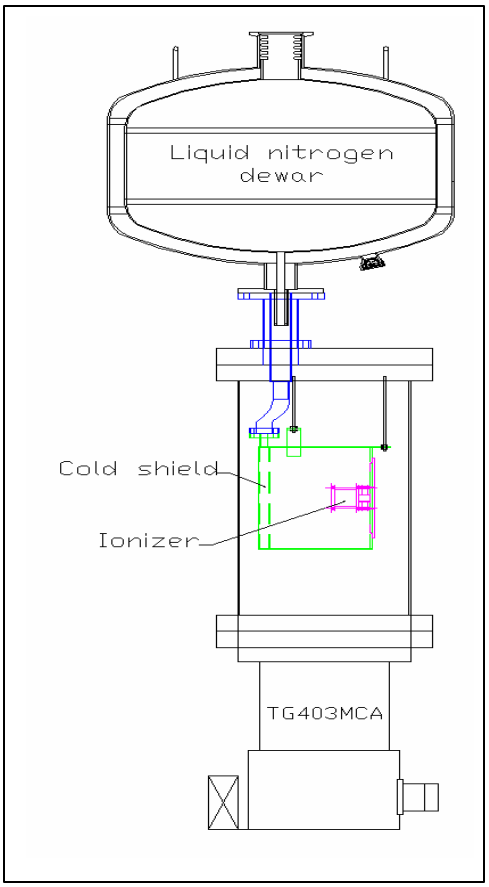

Figure 5: Ultra high vacuum chamber with integrated liquid nitrogen cooling system and ionizer to optimize the heating current versus voltage settings for distinct emission currents and electron energies as low as 7 eV. The feedthrough and the heating wires are omitted for clarity.

4. Personnel Associated with the Research Effort

During this reporting period, postdoctoral fellow Dr. Fangtong Zhang was supported on the AFOSR grant. He designed the tunable electron impact ionizer and also conducted the crossed beams reaction of boron atoms with allene. He will also be available for the AFOSR grant W911NF-05-1-0448. Secondly, Edwin Kawamura (Staff Scientist, University of Hawaii) was available for this project; Edwin designed and built the control units for the new electron impact ionizer.

5. Publications and Presentations

The boron – allene system is currently being written up and will be submitted to J. Chem. Phys once the energetics of the C_3H_3B have been computed. Also, during this reporting period, the PI attended and presented a poster at the AFOSR Molecular Dynamics Contractor's meeting in Asilomar, CA (May 2005). In addition, an abstract entitled 'Chemical Dynamics of Elementary Reactions of Atomic Boron' has been submitted to the organizers of the 232nd ACS Meeting in San Francisco (September 2006), section '*Chemistry in Extreme Environments*'.

6. Invention Disclosures and Patents Granted

Outside of the results reported in the accomplishment section above, there is nothing further to report here.

7. Honors and Awards

There were no significant honors or awards to report during this period.